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Methane emissions from anaerobic sludge digesters in Mexico: On-site determination vs. IPCC Tier 1 method

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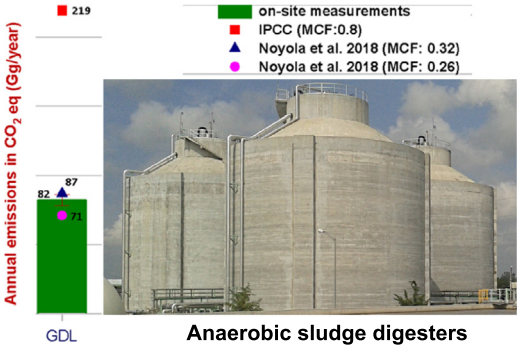
HIGHLIGHTS

- Improved estimates of national CH_4 emission inventories from wastewater are needed.
- A country-specific CH_4 EF for anaerobic sludge digesters is proposed for Mexico.
- IPCC Tier 1 method, with the recommended MCF, generally overestimates CH_4 emissions.
- Tier 1 method using alternate MCF reached closer estimations to on-site emissions.
- It is recommended to adopt the alternate MCF for anaerobic sludge digesters (Tier 1).

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater treatment is an important source of methane (CH_4) emissions. In most large-size aerobic treatment plants, the excess sludge is digested in anaerobic reactors (AD), with the concomitant CH_4 emissions. The guidelines of the Intergovernmental Panel on Climate Change (IPCC) have been adopted worldwide for quantifying the national emission inventories, which include wastewater treatment plants (WWTP) as a key category. The IPCC recommends using default emission factors (Tier 1) for countries with limited available data (such as Mexico and most developing countries). However, these estimates have a high degree of uncertainty, owing to the lack of reliable information about the operation process and local environmental conditions. In order to reduce uncertainty in the estimation of CH_4 emission from WWTP in Mexico, a country-specific emission factor was determined for AD associated with activated sludge process. This was accomplished with on-site data obtained from the AD of six activated sludge WWTP. In addition, the measured CH_4 emissions were compared to those resulting from the application of the IPCC Tier 1 method, using the recommended default methane correction factor (MCF: 0.8) as well as alternate values (0.32 and 0.26) recently proposed by the authors. Results show that the IPCC Tier 1 method, using the recommended MCF, highly overestimate CH_4 emissions compared with the values obtained on-site. In contrast, the alternate MCF achieved better estimations than the IPCC-recommended MCF, much closer to the observed emission values. The CH_4 emission factor proposed as country (Mexico) specific value is 0.49 kg CH_4/kg BOD_{rem}, which would allow the application of IPCC Tier 2 method. By doing so, the uncertainty associated with CH_4 emission from aerobic treatment plants with AD would be reduced. This, in turn, would provide important information for implementing appropriate CH_4 mitigation strategies for the water sector.

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1. Introduction

Wastewater management, from collection to reclamation or final disposal, has been identified as an important source of methane (CH_4) emissions. In fact, sewer systems (Guisasola et al., 2008; Short et al., 2017), wastewater treatment facilities (El-Fadel and Massoud, 2001; Daelman et al., 2012) and sludge management (Hospido et al., 2005; Yoshida et al., 2014) may produce CH_4, depending on the technology applied, the operating conditions and, particularly for sewage networks, ambient temperatures (Noyola et al., 2018).

Methane, a short-lived climate pollutant (SLCP) with an atmospheric lifetime of around 12 years, has a direct influence on climate change, considering its high global warming potential (GWP: 34, according to Myhre et al., 2013), but also has indirect effects, such as its role as a precursor of tropospheric ozone, a powerful greenhouse gas (GHG) (Shindell et al., 2009). At a national level, climate policy measures, such as the National Determined Contributions (NDC), should be supported by using sound data for identifying effective mitigation strategies and monitoring mechanisms. In this regard, efforts should be made to reduce the uncertainties in determining national greenhouse gas inventories. In Mexico and most developing countries, there is a lack of country-specific emission factors for most of the identified key categories.

In the case of wastewater treatment (WWT) and discharge, the guidelines of Intergovernmental Panel on Climate Change (IPCC, 2006) establish the use of default emission factors as a *good practice* for countries with limited data, based on the Tier 1 method for estimating CH_4 emissions. An improvement in the estimation of the national inventories may be achieved if the Tier 2 method is applied. This procedure is basically the same as Tier 1, but incorporating country-specific emission factors at least for the dominant WWT technologies in place, which should be determined based on in-situ measurements.

In fact, the quantification of CH_4 emissions (using default or specific emission factors) is associated with some degree of variability and uncertainty mainly due to the limited data about the operation of the treatment facility and its behavior under varying conditions such as spatial, seasonal, hydraulic and wastewater characteristics (Listowski et al., 2011). In this sense, further research for improving uncertainty analysis in wastewater treatment is needed (Sin et al., 2009). For that matter, the lack of quantitative data of CH_4 emissions from anaerobic sludge digestion (Frijns, 2012), along with the uncertainty and variability of methane production (Bousquet et al., 2006), constitute a priority issue in this sector.

At present, anaerobic digestion is the most commonly applied technology for sludge stabilization in large conventional aerobic municipal wastewater treatment facilities, based on economically and environmental reasons (Hospido et al., 2005; Wang et al., 2011; Molinos-Senante et al., 2014), being an essential part of a modern wastewater treatment plant (WWTP). The use of anaerobic sludge digestion in a conventional activated sludge plant can improve the sustainability of the treatment facility due to biogas production. In fact, when complemented with a combined heat and power (CHP) system, this process constitutes a low-carbon footprint solution for wastewater treatment (Bolzonella et al., 2002; Keller and Hartley, 2003; Bolzonella et al., 2005; Foresti et al., 2006; Hong et al., 2009; Ghosh et al., 2011; Molinos-Senante et al., 2014; Noyola et al., 2016). However, in order to achieve this goal, methane must be well managed, based on good practices, such as optimized digester operation, efficient biogas collection and use, control of CH_4 fugitive emissions, to name the more important issues.

In facilities equipped with anaerobic sludge digestion, this process step can be expected to be a major source of CH_4 (Czepiel et al., 1993; Daelman et al., 2012) due to fugitive emissions and inefficient flaring, contributing about 75% of the WWTP overall methane emission (Listowski et al., 2011). However, in many large treatment facilities, the produced biogas is used in co-generation systems to produce heat and electricity, thus avoiding indirect CO_2 emissions from fossil fuel-derived electricity (Hobson, 1999; Chynoweth et al., 2001; Güereca-Hernández et al., 2015).

According to the Mexican National Water Commission (Conagua, 2016), 120.9 m^3/s of sewage was treated in 2477 municipal WWTP (design treatment capacity: 178 m^3/s). The dominant wastewater treatment technology by number in Mexico is facultative ponds (35.0%) followed by generic activated sludge (30.1%) mostly extended aeration process. From these 745 activated sludge plants, 27 may be identified among the largest, using conventional activated sludge process with anaerobic sludge digesters (López-Hernández et al., 2017), the rest are mostly small and medium-size extended aeration systems. In fact, although second in number, generic activated sludge processes receive 55% of sewage entering a treatment facility in Mexico. Specifically, the 27 facilities with anaerobic digesters treat 44.9 m^3/s (design treatment capacity: 70.6 m^3/s) which represents 37% of the total flow treated in Mexico.

Country-specific emission factors for Mexican anaerobic-facultative ponds have been proposed by Paredes et al. (2015); however, only 11% of the treated flow is carried out by these systems. The availability of a specific emission factor for activated sludge processes associated with anaerobic sludge digestion would increase this coverage to 48%, representing a significant contribution of the IPCC Tier 2 method in estimating CH_4 emission inventories from municipal wastewater treatment in Mexico.

The official Mexican national inventories of GHG from wastewater management are estimated using the IPCC Guidelines (Tier 1) based on default values due to lack of specific activity data and country-specific emission factors. In this case, methane correction factors (MCF) suggested by the IPCC guidelines are applied, simplifying the real situation and generating high uncertainty. In the case of aerobic treatment plants (such as activated sludge processes), those facilities are assumed to work efficiently, and thus the MCF is zero (no emissions) in Mexican inventories. Moreover, no distinction is made between extended aeration and conventional activated sludge with anaerobic sludge digesters, due to lack of reliable information. This approach may lead to a serious underestimation of emissions from this particular treatment process in Mexico.

In order to improve the reliability of the CH_4 emission inventories associated with this important process in Mexico, it is necessary to determine actual CH_4 emissions in full-scale sludge anaerobic digestion systems, considering the operational and environmental conditions of the WWTP. At present, data from full-scale anaerobic sludge digesters are very scarce in Latin America, or hardly available in the grey literature. In such a context, data should be gathered on the field, in order to obtain a specific CH_4 emission factor that may be used for determining the national inventories. As a result, uncertainties will be reduced, allowing policy and decision makers to better evaluate the cost-effectiveness and feasibility of appropriate GHG mitigation strategies for WWT facilities.

The aim of this study was to determine CH_4 emission factors of anaerobic sludge digesters associated with activated sludge process in six full-scale WWTP in Mexico, and to compare the resulting annual emissions to those obtained by the application of the IPCC Tier 1 methodology using the recommended default MCF and the recently proposed MCF values by Noyola et al. (2018).

2. Methodology

2.1. Integration of the sample

The sample studied consisted of six municipal treatment facilities using activated sludge process with anaerobic sludge digestion. In order to consider the diversity of the country, Mexico was divided into three regions (north, central and south). The resulting WWTP are located in the state of Chihuahua (CHI), Nuevo León (MTY), Jalisco (GDL), Querétaro (QRO), San Luis Potosí (SLP) and Veracruz (XAL).

The location of these treatment facilities is presented as Supplementary material (Fig. S1).

The WWT facilities under study have the following process arrangement: preliminary treatment, primary treatment, secondary treatment, effluent disinfection and sludge digestion and disposal (Fig. 1). Preliminary treatment includes bar screens and grit chambers; primary treatment is provided by settling tanks; secondary treatment consists of conventional activated sludge and secondary clarifiers, ending with effluent chlorine disinfection. The excess sludge is thickened and then stabilized in high rate anaerobic digesters (mixed and heated) except for the facilities at CHI and XAL, where heating was not in operation. Digested sludge is disposed in mono-landfills near the treatment facilities. Biogas is burned in flares in all cases, with electricity generation only in GDL and QRO. Wastewater quality data was obtained directly from the operational records (logbook), provided by the plant manager. Relevant data (biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS)), together with general information of the evaluated WWTP are provided as Supplementary material (Table S1).

2.2. Estimated CH_4 emissions – on-site measurements

Two measurement campaigns in each WWTP were accomplished during dry/winter and rainy/summer seasons. Quantification of on-site methane production was done with instantaneous samples taken in the biogas piping of every digester in each facility, as well as in the general line. Data were collected during three days, with a daily sampling frequency of three measurements (morning, afternoon and evening). Methane concentrations were determined using a portable biogas analyzer (Biogas 5000, Geotech, USA, accuracy (vol) ± 0.5%). Total solids (TS), volatile solids (VS) and the percentage of VS in the influent sludge were determined based on data reported in the operation logbook of each WWTP.

2.3. Estimated CH_4 emissions – IPCC methodology

The CH_4 emissions from the digesters in the six facilities were estimated using the Tier 1 method described in the IPCC Guidelines for national inventories of GHG (IPCC, 2006). This methodology is based on default values for the emission factors and on the corresponding influent BOD and treated flow. The equation in the IPCC Guidelines (Vol. 5, Chapter 6, Eq. (6.1)) was simplified for its application to single facilities (Eq. (1)), not considering the term R (amount of CH_4 recovered (or flared) per year (kg CH_4/year)). The reason for doing this was to compare the full CH_4 production from the facilities, independently of the biogas management applied in each one.

$$CH_4 \text{ emissions} = B_o * MCF\,(TOW - S) \quad (1)$$

where B_o is the maximum CH_4 producing capacity per BOD removed (0.6 kg CH_4/kg BOD_{rem}; recommended value) from the wastewater or sludge; MCF is the CH_4 correction factor (0.8 recommended default value for anaerobic digesters); TOW is the total organic matter in wastewater entering the treatment facility per year (kg BOD/year) and S is the organic component (sludge) removed from the facility per year (kg BOD/year). Sludge (as volatile solids, VS) was converted to BOD using the following factors: 1.42 kg COD/kg VS and 2.4 kg COD/kg BOD, resulting in a conversion factor 1.69 kg VS/kg DBO.

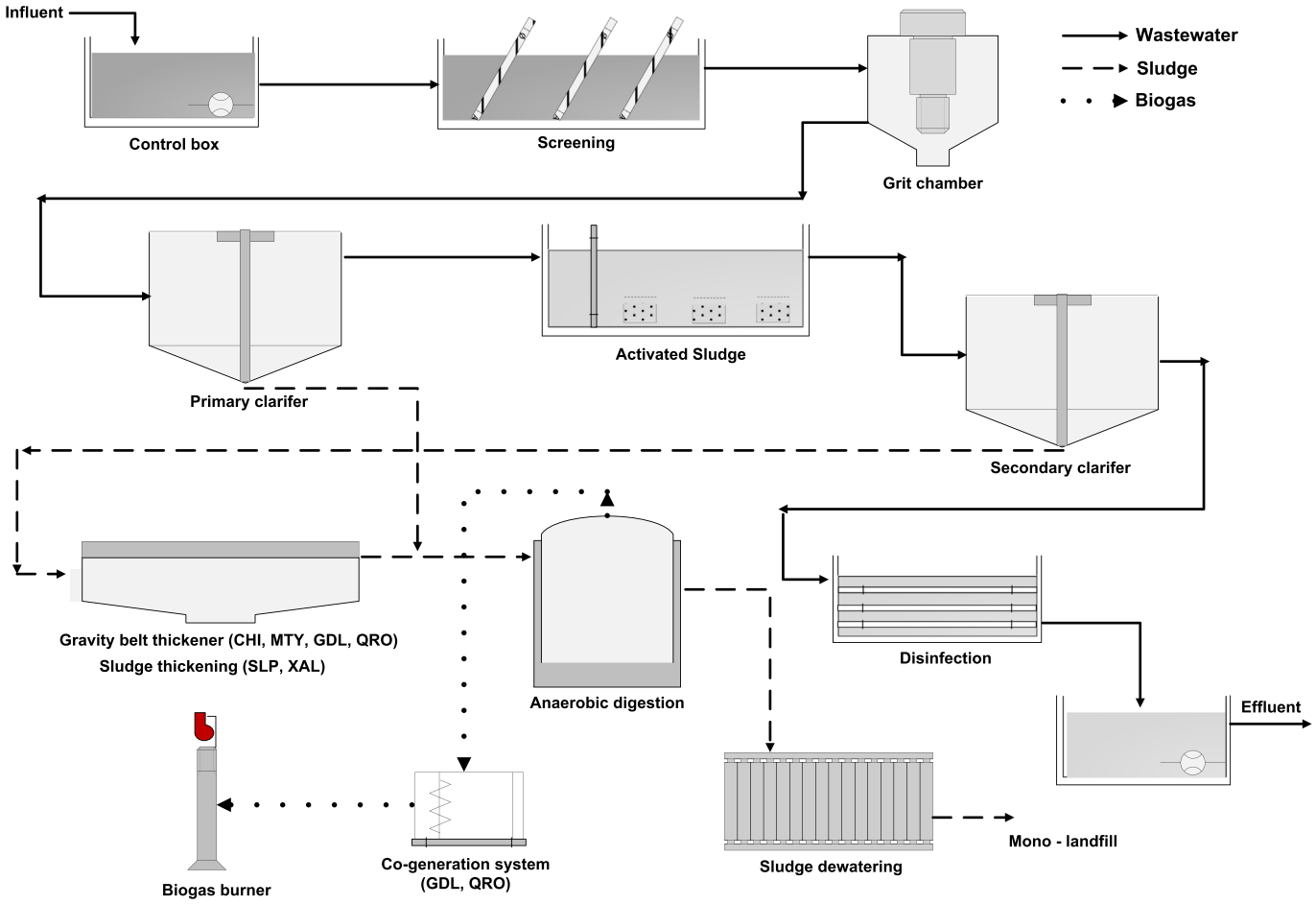

Fig. 1. Common process flow chart for the six evaluated treatment facilities, based on conventional activated sludge with anaerobic digestion.

The default emission factors (EF = B_o * MCF) were obtained using the maximum CH_4 production capacity (B_o) of 0.6 kg CH_4/kg DBO_{rem} and the default MCF (0.8) recommended by the IPCC Guidelines for anaerobic sludge digesters. TOW and S data were taken from Tables S1 and 1. The CO_2 eq. (carbon dioxide equivalent) of CH_4 was calculated using GWP of 34, as reported in the IPCC 5th Assessment Report (Myhre et al., 2013). The calculations are presented in the Supplementary material section.

In addition, alternative estimations were calculated following the same IPCC procedure (Eq. (1)) but using the MCF values recently proposed by Noyola et al. (2018) for WWTP with activated sludge process and anaerobic sludge digestion for Mexico and other intertropical countries (full process: 0.32; anaerobic digesters only: 0.26).

3. Results and discussion

3.1. Performance of the anaerobic digesters and identification of good practices

The sampled WWTP achieved removal efficiencies higher than 80% for BOD, COD and TSS (see Table S1 in the Supplementary material section). GDL facility showed the best treatment performance with 98%, 92% and 96% removal efficiencies, respectively, while SLP had the lowest percent removal with 84, 84 and 81%, respectively. It should be noted the low mean BOD influent concentration (110 mg L^{-1}) in XAL WWTP.

The daily flow and solids content of the excess sludge produced in the six facilities under study are presented in Table 1, together with relevant operational data. Also, methane production and the corresponding emissions expressed as CO_2 eq. determined with field measurements, are included. In four of the facilities (MTY, GDL, QRO and SLP), the heating systems were in operation, providing the expected mesophilic temperatures (32 to 36 °C), positively affecting the digestion process. On the other hand, in the CHI and XAL facilities, the anaerobic digesters were operated at ambient temperature, which corresponds to the lower level of the mesophilic interval (21 to 26 °C), hindering organic degradation and the corresponding CH_4 production (Metcalf and Eddy, 2003).

Solids retention time (SRT) is a critical operating parameter in any biological process. Three of the heated digesters (MTY, GDL and SLP) operate at conservative values, above those applied in practice for high-rate heated digesters (10 to 20 days) according to Metcalf and Eddy (2003), only QRO entering this interval. In the XAL facility, the SRT shows almost a two-fold difference between the design and the actual value (15 vs. 27 d). The low influent BOD concentration in this facility produces excess sludge below the expected design values, resulting in low influent sludge flow and high hydraulic and solids retention times in the digester. In such situation, the high SRT is in agreement with the recommended range for unheated digesters (20 to 30 d) (Metcalf and Eddy, 2003) a consideration that is also met by the other digester working at ambient temperature (CHI) with an SRT of 23 days. On the contrary, in SLP digester, the SRT is highly conservative for a heated reactor, above the typical values.

The TS content in the sludge is in the range of 4.0 to 5.8%, typical values for this type of process (Metcalf and Eddy, 2003). Feeding of dilute raw sludge is a major cause of various negative impacts on digesters operation, among them limited VS removal, reduced CH_4 production and increased heating requirements (Speece, 1988; Bolzonella et al., 2005). However, regarding the volatile content (%VS) in the feed sludge, only GDL and QRO presented the expected values for a raw primary and secondary sludge blend (70 to 80%). CHI and SLP digesters were fed with a mineralized sludge (VS content of 57 and 55% respectively). This characteristic hinders VS removal efficiency and biogas production per ton of TS fed, as limited substrate (organic matter) is available.

Low VS removal efficiencies correspond to the facilities working at a lower temperature (CHI and XAL) as well as to MTY, operating at a sub-optimal mesophilic temperature (32 °C). As a result, a partial sludge stabilization would be expected, particularly in the case of MTY and XAL, fed with a convenient volatile fraction (64 and 65% respectively). Generally, in a typical mesophilic anaerobic high rate digestion process, 40 to 45% (Hobson, 1999) or even 45 to 65% (Metcalf and Eddy, 2003) volatile solids are removed, depending on the sludge retention time, the operating temperature and the mineral content of the raw waste. The GDL, QRO and SLP digesters achieve volatile solids removals at the lower limit of this interval.

Biogas is only used in two WWTP (GDL and QRO) in a combined heat and power equipment that generates 50 to 60% of the overall electricity demand of the facilities. As fossil fuels are the major component (82.1%) in the electricity mix in Mexico (SENER, 2015), replacing electricity consumption from the grid will reduce indirect GHG emissions from WWTP. In the other four facilities (CHI, MTY, SLP and XAL), biogas is just burned in flares.

Based on the aforementioned discussion, it is possible to identify that QRO and GDL facilities are applying good sludge digestion practices. MTY is closed to this situation, limited by its operation at the lower end (32 °C) of the optimal mesophilic temperature interval and the limited volatile solids removal attained (31%), while SLP works at a very high SRT (excessive capacity) with mineralized influent sludge (55%). On the contrary, CHI and XAL digester are not operated under good practices, mainly due to the low temperature of the anaerobic reactor (26 and 21 °C respectively). In general, in the case of digesters working below the expected performance, improvements should be focused on the raw sludge digestibility, digester configuration and process control and stability (Ahring, 2003). Addition of metallic micronutrients may also be an effective measure in such cases (Speece, 1988).

Table 1
Solids content in sludge and relevant operational data of the anaerobic digesters with the resulting methane production for the six WWTP.

Feeding sludge characteristics	Units	CHI	MTY	GDL	QRO	SLP	XAL
Influent sludge	m^3/d	904 ± 107	2741 ± 304	1070 ± 131	460 ± 85	239 ± 75	231 ± 71
Total solids (TS)	g/L	39.8 ± 7.5	42.8 ± 4.9	57.9 ± 7.1	47.2 ± 7.8	55.8 ± 14	43.4 ± 7
Volatile solids (VS)	g/L	22.5 ± 3.3	27.3 ± 2.5	40.4 ± 4.5	32.9 ± 3.5	30.7 ± 4.7	28 ± 5.4
Volatile fraction	%	57	64	70	70	55	65
Digester							
Total digestion (useful) volume	m^3	20,628	61,365	23,206	8500	7360	6160
Number of digesters	unit	3	5	3	2	2	1
Solid retention time (SRT) (design)	days (d)	23	15	16	16	30	15
Solid retention time (SRT) (actual)	days (d)	23	22	22	18	31	27
Operational temperature	°C	26 ± 4	32 ± 2	36 ± 3	33 ± 2	35 ± 2	21 ± 2
% VS removal	%	24 ± 9	31 ± 4	54 ± 1.2	40 ± 6	39 ± 6	23 ± 6
Biogas production[a]	m^3/d	4047 ± 247	39,608 ± 1642	13,744 ± 683	5205 ± 461	3880 ± 204	700 ± 101
CH_4 content in biogas	%	64.9 ± 1.2	65.9 ± 1.3	67.4 ± 0.8	65.5 ± 2.4	63.3 ± 2.5	61.6 ± 3
CH_4 production[a]	m^3 CH_4/d	2626 ± 160	26,102 ± 1082	9264 ± 460	3409 ± 302	2456 ± 129	431 ± 62
CO_2 eq.	Gg/year	23 ± 1.4	232 ± 10	82 ± 4	30 ± 3	22 ± 1.2	3.8 ± 0.6

[a] Reported at 273 K and 1 atm.

3.2. Methane emission factors for the six WWTP evaluated

Based on the field data, Table 2 presents the CH_4 emission factors obtained for the anaerobic digesters in each WWTP sampled. Data shown include CH_4 emission factors expressed with the conventional units (kg CH_4/kg DBO_{rem}) and based on VS removed. In addition, these values are converted to volume (normal conditions) of CH_4 (m^3 CH_4/kg VS_{rem}) and on the basis of VS fed (m^3 CH_4/kg VS_{fed}). It may be noted that the values obtained for MTY and SLP (emission factors in parentheses) are much higher than the expected upper limit indicated by the stoichiometry of the oxidation of CH_4: 0.25 kg CH_4/kg COD or 0.6 kg CH_4/kg BOD_{rem}. These are the default values for B_o, the maximum CH_4 producing capacity in Eq. (1) (IPCC, 2006).

There is no clear explanation for the incongruent emission factors calculated for MTY and SLP. Apparently, the registered biogas (methane) produced daily at those facilities do not correspond to the VS load removed. A comparative analysis of data in Tables S1 and 1, supported by data in Fig. 2, which will be discussed in the next section, may confirm that the inconsistencies are due to two different factors. In the case of MTY facility, the low VS removal efficiency (31%) obtained from the facility's logbook (Table 1) could be underestimated. In SLP facility, apparently, the raw sludge flow is underestimated, based on the organic load treated in that WWTP and the low S/TOW ratio (as per Eq. (1)) as presented in the Supplementary material. In this regard, it should be mentioned that the factor used for converting sludge from VS basis to BOD (1.69 kg VS/kg DBO) as presented in Section 2.2, does not take into consideration differences in the composition of the organic fraction in the sludge produced in the treatment facilities.

CH_4 emission factors may fluctuate over a wide range, depending on the volatile solids content of the sludge fed and the biological activity in the digester, which in turn is the result of several operational variables (Lin et al., 1997; Metcalf and Eddy, 2003). The CH_4 emission factors obtained in this study are in the range of 0.07 to 0.35 m^3 CH_4/kg VS_{fed} and 0.29 to 1.13 m^3 CH_4/kg VS_{rem}. As shown in Table 3, the last interval is in agreement with the typical range reported in the literature for CH_4 conversion (emission) factors of anaerobic sludge digesters (0.13 to 1.0 m^3 CH_4/kg VS_{rem}), excepting the highest values in Table 2 (MTY: 1.13), an issue that has been discussed above.

The higher conversion factors (MTY and SLP) are related to digesters that do not operate under good practices if compared with the QRO and GDL facilities. As mentioned above, MTY works at a suboptimal temperature (32 °C) and SLP at an excessive SRT (31 d) for a mesophilic digester. Based on these considerations, a CH_4 emission factor between 0.49 and 0.68 kg CH_4/kg DBO_{rem} may be recommended for anaerobic sludge digesters in Mexico, the lower value being preferred due to stoichiometry reasons. The adoption of this country-specific emission factor would result in the application of the IPCC Tier 2 method, improving the Mexican greenhouse gas inventory from wastewater treatment. In addition, based on similar technological and socio-economical contexts, this emission factor may also be applied in other Latin American countries.

On this regard, Cohen (2017) revised the different approaches taken by four Latin American countries (Brazil, Chile, Colombia and Peru) for preparing their national emission inventories from wastes. The author identified that the IPCC methods applied in each country varied on the generalization degree of the wastewater treatment processes and the use of limited country-specific information. Based on the scarce data available in those countries, the study concludes that a greater degree of resolution in information and more locally-specific data will lead to results that better represent the actual emissions from a particular country. The emission factor here proposed, together with the alternate MCF (Noyola et al., 2018) may be considered as contributions for meeting such demand.

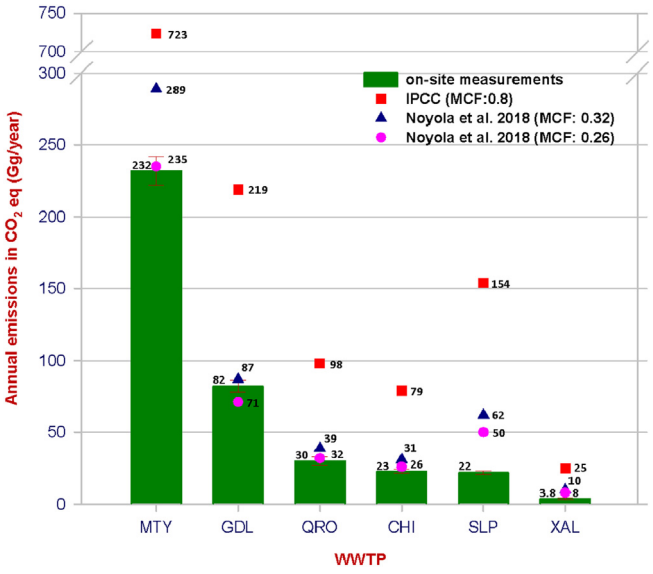

Fig. 2. Comparison of annual methane emissions as CO_2 eq. from the anaerobic digesters in six WWTP evaluated, based on the IPCC methodology (Tier 1) using the recommended value (MCF = 0.8), the MCF proposed by Noyola et al. (2018) for aerobic full treatment facilities (0.32) and for anaerobic sludge digesters only (0.26) and the data obtained on-site.

3.3. Comparison between emissions based on MCF and on-site measurements

The annual CH_4 emissions as CO_2 eq. for the six anaerobic digester facilities are presented in Fig. 2, using the IPCC default MCF (0.8, as recommended for Tier 1 calculation) and the actual data measured on-site. It should be mentioned that the IPCC related values refer to the full treatment facility and not only to the anaerobic digesters, as Eq. (1) was used for calculating those emissions. However, according to the IPCC guidelines, a well-managed centralized aerobic WWTP does not emit CH_4, so those values are suitable for comparison purposes.

The estimated CH_4 emissions using IPCC-Tier 1 are much higher than the on-site measurements in each of the six WWTP analyzed. The overestimation of CH_4 emissions from the six treatment facilities using IPCC Tier 1 method, is consistent with the results obtained by El-Fadel and Massoud (2001), Monteith et al. (2005), Paredes et al. (2015) and Delre et al. (2017) while evaluating different treatment processes. For the specific case of activated sludge process, the Tier 1 approach (using Eq. (1) and 0.8 as MCF) assumes that in an anaerobic sludge digester, 80% of the organic matter (BOD) removed by the WWTP is

Table 2
Methane emission factors obtained for the anaerobic digesters in the six WWTP evaluated (at normal conditions: 273 K and 1 atm).

Emission factor	Units	CHI	MTY	GDL	QRO	SLP	XAL
CH_4 emission factor[a]	kg CH_4/kg DBO_{rem}	0.66	(1.38)	0.49	0.68	(1.05)	0.35
CH_4 emission factor per VS removed	kg CH_4/kg VS_{rem}	0.39 ± 0.02	0.81 ± 0.10	0.29 ± 0.01	0.40 ± 0.04	0.62 ± 0.04	0.21 ± 0.04
CH_4 emission factor per VS removed	m^3 CH_4/kg VS_{rem}	0.54 ± 0.03	1.13 ± 0.14	0.40 ± 0.02	0.56 ± 0.05	0.86 ± 0.05	0.29 ± 0.05
CH_4 emission factor per VS fed	m^3 CH_4/kg VS_{fed}	0.13 ± 0.03	0.35 ± 0.05	0.21 ± 0.01	0.23 ± 0.02	0.34 ± 0.05	0.07 ± 0.02

[a] Emission factor based on the corresponding kg CH_4/kg VS_{rem} value after converting kg VS to kg BOD (see Section 2.2).

Table 3
CH_4 conversion (emission) factors from sludge anaerobic digesters in full-scale activated sludge facilities with associated relevant data.

Reference	m^3 CH_4/kg VS_{rem}	Temperature (°C)	SRT (days)	VS removal (%)
Speece, 1988	0.13–1.0	16–39	5–30	23–82
Bolzonella et al., 2002	0.4–0.9	33–37	19–21	16–23
Dohányos et al., 2004	0.73	35	11	44
Bolzonella et al., 2005	0.5–0.9	35–37	20–40	13–27
Geshnigani, 2013	0.45–0.55	35–37	21	59–68
This study	0.29–1.13	21–37	18–31	23–54

converted to CH_4. As discussed by Noyola et al. (2018), the IPCC guidelines are ambiguous about the procedure for estimating CH_4 emissions from WWTP using aerobic processes for wastewater treatment coupled with anaerobic reactors for sludge digestion. In such process, instead of recommending a two-step calculation, separating the emissions from the water and the sludge lines with the corresponding MCF, a choice should be made between "centralized, aerobic treatment plant" and "anaerobic digester for sludge" (recommended MCF 0.0 and 0.8 respectively). The selected procedure should consider the main source of CH_4 (i.e., the anaerobic digesters), so the MCF will be 0.8. However, as pointed-out by Noyola et al. (2018), this approach drastically overestimates CH_4 emissions, as the value of TOW considered in Eq. (1) represents the total BOD removed by the treatment facility, not only by the digester. In this regard, the data published by Delre et al. (2017) show that the estimated emissions from five WWTP in Denmark and Sweden based on the IPCC Tier 1 methodology were 5 to 29-fold higher than those measured using the tracer ratio release method. To address this biased calculation, Noyola et al. (2018) proposed a new entry in the IPCC guidelines, referring to a "centralized, aerobic treatment plant with anaerobic sludge digesters" with an MCF of 0.32, together with an MCF of 0.26 for anaerobic sludge digesters alone.

In addition to the above mentioned limitations, the IPCC Tier 1 general approach may overestimate the actual CH_4 production as it does not take into consideration several factors, such as the process operating conditions, specific urban-geographical characteristics of the population served, physicochemical interactions, biological inhibition, nutrient limitation, degree of decomposition in the digestion process, etc. (El-Fadel and Massoud, 2001; Abdelgadir et al., 2014). As a result, the IPCC Tier 1 estimation is imprecise and may not provide a reliable basis for the identification of priorities and the development of effective strategies to reduce GHG emissions from wastewater treatment facilities (Monteith et al., 2005).

On the other hand, bottom-up calculations, such as the on-site data approach presented in this study, is based on the quantification of methane at the digestion facilities, which are operated under real conditions, thus taking into account diverse environmental and operational factors that directly influence CH_4 production. Another issue of disagreement between general approaches using default values and on-site measurements can be related to biogas leakages in the anaerobic digestion and biogas handling equipment (Czepiel et al., 1993; Daelman et al., 2012; Yoshida et al., 2014; Noyola et al., 2018). The data from the operation logbook only include the measured biogas, so leaks are not considered as they are unknown. Other methods, such as the tracer ratio release, should be applied to quantify this unaccounted fraction (Lamb et al., 1995; Mønster et al., 2014; Yver et al., 2015; Delre et al., 2017). However, at present, the high cost of the analytical equipment associated with this method hinders its implementation as a monitoring option in the treatment facilities, even the largest ones.

As mentioned, alternative MCF have been proposed for improving the results obtained by the Tier 1 method and its default MCF, focusing on activated sludge processes with (0.32) and without (0.06) anaerobic sludge digesters (Noyola et al., 2018). The CH_4 emissions estimations (as CO_2 eq.) using the proposed MCF for the full process (activated sludge and anaerobic digesters: 0.32) and only for the anaerobic digesters (0.26) are presented in Fig. 2. In all cases, the gap between the on-site measurements and the estimated emissions is significantly reduced, compared with the values obtained using the MCF proposed by the IPCC guidelines (0.8). The actual emissions are very well estimated with the MCF associated with the anaerobic digesters, as this is a direct comparison; the major difference is found for SLP facility (a possible explanation for this inconsistency has been presented in Section 3.2). The values obtained with the MCF for the full process are also very close to the on-site measurements, the difference being associated with other CH_4 emissions sources, particularly the dissolved CH_4 in the raw sewage entering the WWTP. In consequence, the MCF proposed by Noyola et al. (2018) may produce a more precise estimation and therefore might be adopted in the national greenhouse gas inventories associated with the wastewater treatment activity when applying the IPCC Tier 1 method.

4. Conclusions

CH_4 emissions from anaerobic sludge digestion using the IPCC Tier 1 method presented an overestimation concerning the values obtained on-site at six full-scale treatment facilities in Mexico. In contrast, the results obtained with the Tier 1 method, but applying an alternate MCF (0.26 and 0.32), were much closer to the actual values determined on-site.

The CH_4 emission factors determined in the GDL and QRO facilities (0.49 and 0.68 kg CH_4/kg DBO_{rem}, respectively) may be considered as representative of anaerobic sludge digestion associated with activated sludge processes with good operational practices in Mexico. Based on the stoichiometry of methane oxidation, 0.49 kg CH_4/kg DBO_{rem} may be recommended as country-specific emission factor for Mexico.

The on-site CH_4 emission factor here obtained allows the IPCC Tier 2 application for the calculation of national GHG inventories for activated sludge processes associated with anaerobic sludge digesters in Mexico. As a result, uncertainty may be reduced in the corresponding inventories, and improved technical assessments may be attained for identifying more effective mitigation actions in the water sector.

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Appendix A. Supplementary data

Supplementary material on the characteristics and treatment performance of the six WWTP evaluated, and on the application of Eq. (1) using the different MCF can be found in the on line version of this paper. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.11.373.

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